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PATENT
0641-0255P

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicant:	Walter Henry BERRYMAN	Conf.:	4113
Appl. No.:	10/694,888	Group:	
Filed:	October 29, 2003	Examiner:	
For:	CIRCUITS INCLUDING A TITANIUM SUBSTRATE		

LETTER

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

March 30, 2004

Sir:

Under the provisions of 35 U.S.C. § 119 and 37 C.F.R. § 1.55(a), the applicant(s) hereby claim(s) the right of priority based on the following application(s):

Country	Application No.	Filed
AUSTRALIA	2002952359	October 30, 2002
AUSTRALIA	2003900272	January 20, 2003

A certified copy of the above-noted application(s) is(are) attached hereto.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fee required under 37 C.F.R. §§ 1.16 or 1.17; particularly, extension of time fees.

Respectfully submitted,

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JMS/ndb
0641-0255P

Attachment(s)

(Rev. 02/12/2004)

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0641-0255P
10/694,888
October 29, 2003
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1 of 2

Patent Office
Canberra

I, JANENE PEISKER, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2002952359 for a patent by HYBRID ELECTRONICS AUSTRALIA PTY. LTD. as filed on 30 October 2002.

WITNESS my hand this
Seventh day of November 2003

J. K. H.

JANENE PEISKER
TEAM LEADER EXAMINATION
SUPPORT AND SALES

HYBRID ELECTRONICS AUSTRALIA PTY. LTD.

COMMONWEALTH OF AUSTRALIA

Patents Act

PROVISIONAL SPECIFICATION FOR THE INVENTION ENTITLED:

CIRCUITS INCLUDING A TITANIUM SUBSTRATE

This invention is described in the following statement:

CIRCUITS INCLUDING A TITANIUM SUBSTRATE

The present invention relates to electronic circuits including thick-film hybrid circuits that are constructed on or include a metallic substrate.

The present invention is related to provisional patent application PS0110 filed 23 January 2002, the disclosure of which is incorporated herein by cross-reference.

The present invention may provide a process for manufacturing thick-film hybrid electronic circuits on or including titanium or titanium-alloy substrates. Throughout the specification, the term "titanium" is to be interpreted to include titanium-based alloys, as well as various "commercially pure" grades of titanium metal.

The present invention may include a process that allows dielectric layers and conductive inks to be fired without causing excessive curvature of the metallic substrate. The present invention may also include a process that promotes good adhesion between the dielectric layers and the substrate.

As discussed in patent application PS 0110, thermal-expansion coefficients of materials used in manufacturing thick-film hybrid-circuits that are constructed on or include a metallic substrate must be fairly similar, to avoid high mechanical stresses being produced in the materials as the circuit cools after printed layers of the circuit are fired. Unless the stresses are controlled, they will cause bending of the manufactured circuit, and may cause fracture of glass-like layers formed during the firing. Furthermore, stresses which build up in resistive layers tend to cause unwanted variations in electrical properties of resistors within a manufactured circuit.

While stainless steel has been used as a hybrid-circuit substrate material (refer US Patent 6,233,817), particularly for heating elements and associated electronic circuits, the use of titanium is new, and there is no established range of dielectric and resistive inks available specifically for use with titanium.

Accordingly, one aspect of the present invention may identify processing steps and combinations of commercially-available materials that may be compatible with thermal-expansion properties associated with titanium substrates. It may be noted that various grades of titanium and its alloys provide a relatively wide range of temperature coefficients of expansion, so that there may not be a unique recipe that fits all cases. The temperature coefficient of expansion is not constant over the range between ambient room temperature and the firing temperature. In other words, expansion is nonlinearly related to temperature. As far as substrate bending and thermally-induced stresses are concerned, the main concern is relative contractions that occur as the materials cool towards ambient temperature from the solidification-point of each glassy layer.

Titanium metal surfaces are normally covered with a thin oxide layer, which protects the metal from further corrosion. The oxide closest to the metal has a different composition to that in contact with the atmosphere. When titanium is heated in a furnace, as it is in the manufacture of a thick-film hybrid circuit, the oxide layer tends to grow in thickness.

When dielectric pastes are printed onto a titanium substrate and fired in a furnace, typically at temperatures of 800 to 850 °C, the paste fuses into a glassy layer. More than one such layer may be used, to provide high dielectric strength, for example. Some components of the dielectric material may diffuse through the titanium oxide layer during firing. Another effect, seen with some dielectric materials, is formation of voids at the interface between the fused dielectric and the titanium or titanium oxide layer. Generally, the formation of voids is undesirable, as it may lead to poor adhesion between the dielectric and the substrate. Diffusion of dielectric components, such as lead compounds, may be beneficial in promoting adhesion.

When the fired substrate is cooled, some strain relief occurs in titanium due to annealing, in the range 500 to 600 °C.

The present invention may provide a process by which desirable properties in the manufacture of a thick-film hybrid circuit on a titanium substrate may be achieved.

The present invention may provide a process for manufacturing thick-film hybrid circuits on a titanium or titanium-alloy substrate with glassy dielectric layers fired upon one or both surfaces of the metal. The process may include lead diffusion through titanium oxides on the metal surface to form a strong bond between the metal substrate and the dielectric layer immediately adjacent to it. The process may include firing of additional layers of similar or different dielectric material on top of the dielectric layer immediately adjacent the substrate. The process may include steps such that bending experienced by the hybrid circuit is controlled by selection of materials and layer-thicknesses according to their associated temperature coefficients of expansion and Young's modulus. A layer of dielectric material may be placed on the reverse side of the substrate to inhibit growth of oxide during firing. The reverse-side dielectric layer may be removed after some or all of the firing processes are complete. Alternatively, the reverse-side dielectric layer may be left in place after the firing processes are complete. The process may include steps such that bending of the finished thick-film hybrid circuit is controlled by modification of the firing temperatures of the various layers. The process may include steps in which temperature coefficients of resistivity of circuit elements including resistors, thermistors or strain gauges, are controlled by arrangement of dielectric layers upon which they are printed, including layers that may be printed on top of these elements. The process may include steps in which the temperature coefficient of resistivity of a strain gauge may be controlled by proportions of different dielectric inks, mixed together before firing and used to produce the layer or layers upon which the strain-gauge material is printed and fired.

In one embodiment a first step is to print and fire a dielectric ink, typically one such as Metech 7600A, on a cleaned titanium surface. The resulting dielectric is a glassy material with some lead content. During firing, some of the lead may diffuse through the oxide and into the titanium surface, providing a mechanically strong bond between the dielectric and the substrate. This interface-layer

composition has been verified by scanning electron microscopy of sample cross-sections. The dielectric mentioned above is intended by its manufacturer for use on alumina substrates, and its temperature coefficient of expansion is about 7×10^{-6} per °C, and is approximately matched to that of alumina (about 6.4×10^{-6} per °C).

The strength of the dielectric-to-titanium bond has been verified by the following "peel" test. A large component, such as a tab-mounted integrated-circuit voltage regulator, is soldered to a conductive pad printed and fired on a completed hybrid circuit. Mechanical force is then applied to separate the component off the hybrid circuit, and the circuit is inspected to determine where separation has occurred: dielectric-to-substrate, between dielectric layers, dielectric-to-conductor, or conductor-to-solder. The amount of force required to separate the layers is an indication of the bond strength between the layers that separate.

A second dielectric layer is then printed and fired on top of the first. Typically this is a material such as Electro-Science Laboratories' insulating composition 4924, which is intended for use in manufacturing of heating elements, deposited on stainless steel grade 430. One reason for choosing this material is that its temperature coefficient of expansion, (approximately 8×10^{-6} per °C) is a better match to that of titanium and its alloys (about 9.7×10^{-6} per °C over 20° to 500°C) than the temperature-coefficients of dielectrics designed for use on alumina substrates. Another reason is that adhesion of printed conductors to 4924 is much better than their adhesion to 7600A. More than one layer of 4924 material can be successively printed and fired, depending on the final dielectric thickness and dielectric strength required.

In some applications, the choice of dielectric material may be important because it affects the temperature coefficient of resistivity of circuit elements, such as resistors, thermistors and strain gauges, printed and fired on top of the dielectric layers. The present invention may enable relatively close control of properties of such circuit elements. The selection and layering of dielectric materials may be used to control and to tailor these properties. Dielectric

material may also be printed on top of printed circuit elements, typically as a protective layer. When a top dielectric is used, it may also be part of the mechanism for controlling the temperature coefficients of the underlying circuit elements.

Because the temperature coefficients of both dielectric materials are lower than that of titanium, it may be expected that a dielectric-coated face of the substrate would be convex after cooling, as illustrated in Fig. 1. Convexity should be due to the titanium substrate contracting more than the dielectric layers as it cools, so that the titanium would be mainly in tension and the dielectric would be wholly in compression. Fig. 1 includes a graphical representation of an idealised distribution of stress across a cross-section of the cooled circuit.

In practice, it is found that a hybrid circuit manufactured as described above may curve in the opposite direction to that shown in Fig. 1. This is evidently due to formation of an oxide layer on the bottom surface of the titanium when it is fired. Images obtained from secondary electron microscopy confirm that a TiO_2 layer, typically of 10 μm thickness, is formed during the first firing. Repeated firings, required to form additional layers of dielectric or other materials on the top surface, cause the thickness of the bottom-surface oxide layer to increase. Reported values for the temperature coefficient of expansion of titanium dioxide vary (refer Lynch et al, "Engineering Properties of Selected Ceramic Materials", American Ceramic Society, Columbus, Ohio, 1966), but is about 8.8×10^{-6} per °C. This is significantly below that of titanium. Fig. 2 shows a representative stress distribution for this situation.

In order to prevent the growth of oxide on the bottom surface of the substrate, the present invention may include use of a layer of material, such as a dielectric ink, to coat the bottom surface of the substrate.

This bottom-surface coating layer may be used in either of two ways. Firstly, it may be regarded as a sacrificial layer, whose purpose is solely to prevent growth of bottom-surface oxide during firing of the top-surface layers. In this

case, the sacrificial layer would be removed after the sequence of firings is complete, using abrasive or chemical means.

Alternatively, the bottom-surface coating layer may be left in place after completion of the firing-sequence, becoming part of the finished hybrid-circuit device. In this case, the residual stresses in the bottom layer, as well as those in the top layers and the substrate itself, may determine the radius of bending in the finished device.

Experiments have shown that the degree of bending that results from firing and cooling depends to some extent on the temperature at which firing is performed. While it is common to fire dielectric materials at 850°C, noticeably reduced bending is obtained with a firing temperature of 800°C, which is still high enough for some dielectric materials. The present invention may include manipulation of firing temperature as an additional means of controlling bending of manufactured thick-film circuits on titanium substrates.

When strain gauges are printed and fired on top of dielectric layers, the temperature coefficient of resistance of the gauges preferably are small in magnitude, because variation of resistance due to strain tends to be confounded by resistance-variation of due to temperature-change. For example, it has been found that printing ESL strain-gauge ink type 3414A on top of ESL dielectric 4924 over a titanium substrate produced a higher resistivity than the same material printed on alumina. The temperature coefficient of resistance was about -150×10^{-6} per °C. Printing the same strain-gauge ink on top of Metech dielectric type 7600A over titanium produced a lower resistivity than on alumina, but with a positive temperature coefficient of about 200×10^{-6}. Mixing the two dielectric pastes gave an intermediate result, with the implication that the temperature coefficient of thick-film strain-gauges can be reduced to a low magnitude by controlling the proportions of these or other dielectric materials.

Finally, it is to be understood that various alterations, modifications and/or additions may be introduced into the constructions and arrangements of parts previously described without departing from the spirit or ambit of the invention.

DATED: 30 October, 2002

PHILLIPS ORMONDE & FITZPATRICK
Attorneys for:
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David B Fitzpatrick

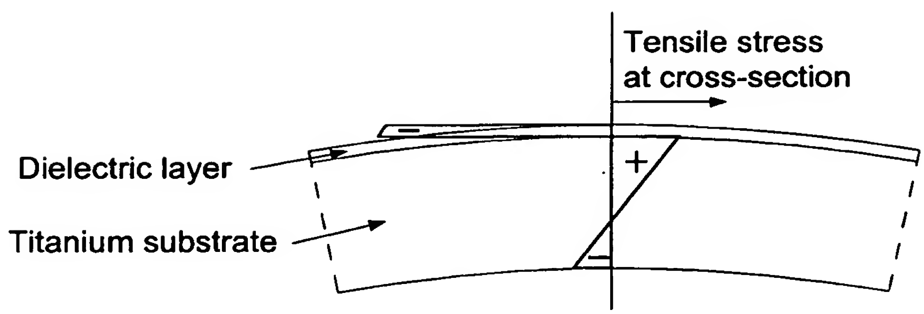

FIGURE 1

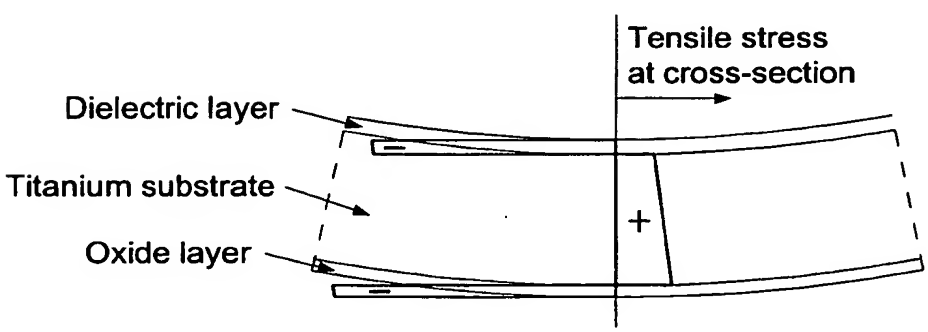

FIGURE 2